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## PREDICTIVE ECOLOGICAL RISK ASSESSMENT OF GRAPHITE INFRARED WAVELENGTH OBSCURANT IN A TERRESTRIAL ENVIRONMENT



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## EXECUTIVE SUMMARY

The U.S. Army is currently developing military hardware and methodology to disseminate obscurants that attenuate light in the infrared (IR) wavelengths. While obscurant testing has been ongoing for several years more routine and widespread testing for training purposes may occur after the type classification of several currently experimental models. In an effort to predict the potential ecological impact of this testing, and hence reduce costly cleanup later, the Joint Projects Office has sponsored this work to develop methodologies for conducting Predictive Ecological Risk Assessments (ERA) for developmental smoke materials. This process follows guidelines recommended by the U.S. Environmental Protection Agency (EPA) for conducting an ERA. ERAs are most often applied to clean-up sites and Base Realignment and Closure (BRAC) procedures but will be adapted here to predict and possibly prevent adverse environmental impact from military obscurant testing.

This ERA is intended to be a screening level or tier-one assessment. Its purpose is to investigate the body of literature and data available, assess potential impact based on current information, identify data deficiencies and recommend additional investigations required in making a scientifically sound predictive assessment. This document assumes little or no experience in Ecological Risk Assessment, the format introduces the reader to aspects of how an ERA is intended to function, it therefore may contain more explanatory narration than in ERAs written for an experienced audience.

There is limited environmental toxicity and exposure data available relating to the effect of graphite on ecological systems. This may be due in part to the accepted low toxicity of the material based on its chemical makeup and the relatively unique application the Army has for the material. Other than testing conducted by the Army or its contractors there is little corroborative information on the subject of terrestrial environmental toxicity. Model data is presented on graphite concentration and deposition rates from one type of recently type classified large area obscurant disseminator, the M56. Several studies are reviewed that assess the toxicity of graphite to plants, soil invertebrates and laboratory rats. In general these studies indicate that, in comparison to other smoke materials, graphite represents a limited threat to a terrestrial environment. The Risk Characterization section of this document quantifies the anticipated risk testing with graphite material may have on the terrestrial environment and identifies current data gaps and the types of research recommended for any additional testing.

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# **PREDICTIVE ECOLOGICAL RISK ASSESSMENT OF GRAPHITE INFRARED WAVELENGTH OBSCURANT IN A TERRESTRIAL ENVIRONMENT**

## **1. INTRODUCTION**

For many years the U.S. Army at ERDEC (formerly CRDEC) and other locations has been developing field systems to disseminate various specialty obscurant materials (Savage, 1992). Historically smokes were aimed at attenuating light in the visible wavelength to protect troop and military vehicles from visually cited weapons. Traditionally these smokes included phosphorus based materials, hexachloroethane (HC) and most recently fog oil (FO). With a conscious effort to lessen the impact on human and environmental health effects fog oil has become the most widely accepted visual screening material at training and development sites.

The advent of more advanced weapons systems containing sophisticated target acquisition and guidance systems spurred the development of smokes that attenuate light in the infrared (IR) and millimeter (MMW) wavelengths. The most popular IR smokes are solid materials of brass or graphite flakes. Most MMW smoke systems are still in development and are not considered in this document.

Since personnel training and hardware development often involves environmental release of these smokes/obscurants it's important to understand the impact these materials may have from a human and environmental health standpoint. Since policy makers and environmental regulators are tightening restrictions on any activities that may adversely affect the environment, an Ecological Risk Assessment (ERA) will help identify any potential problems associated with the activity. Used in this manner, an ERA is a process that evaluates the likelihood that an activity resulting in release of an environmental stressor will result in adverse effects. A risk does not exist unless (1) the stressor has the inherent ability to cause one or more adverse effects and (2) it co-occurs with or contacts an ecological component (ie., organism, populations, communities, or ecosystems) long enough and at sufficient intensity to cause an identified adverse effect. An ERA may evaluate the effect of one or more stressors and one or more ecological components. For this ERA a single stressor, "graphite" will be evaluated against several ecological components characteristic of a terrestrial environment. A description of ecological components and approaches used in conducting this assessment will be discussed in the introduction and problem formulation sections.

## 1.1

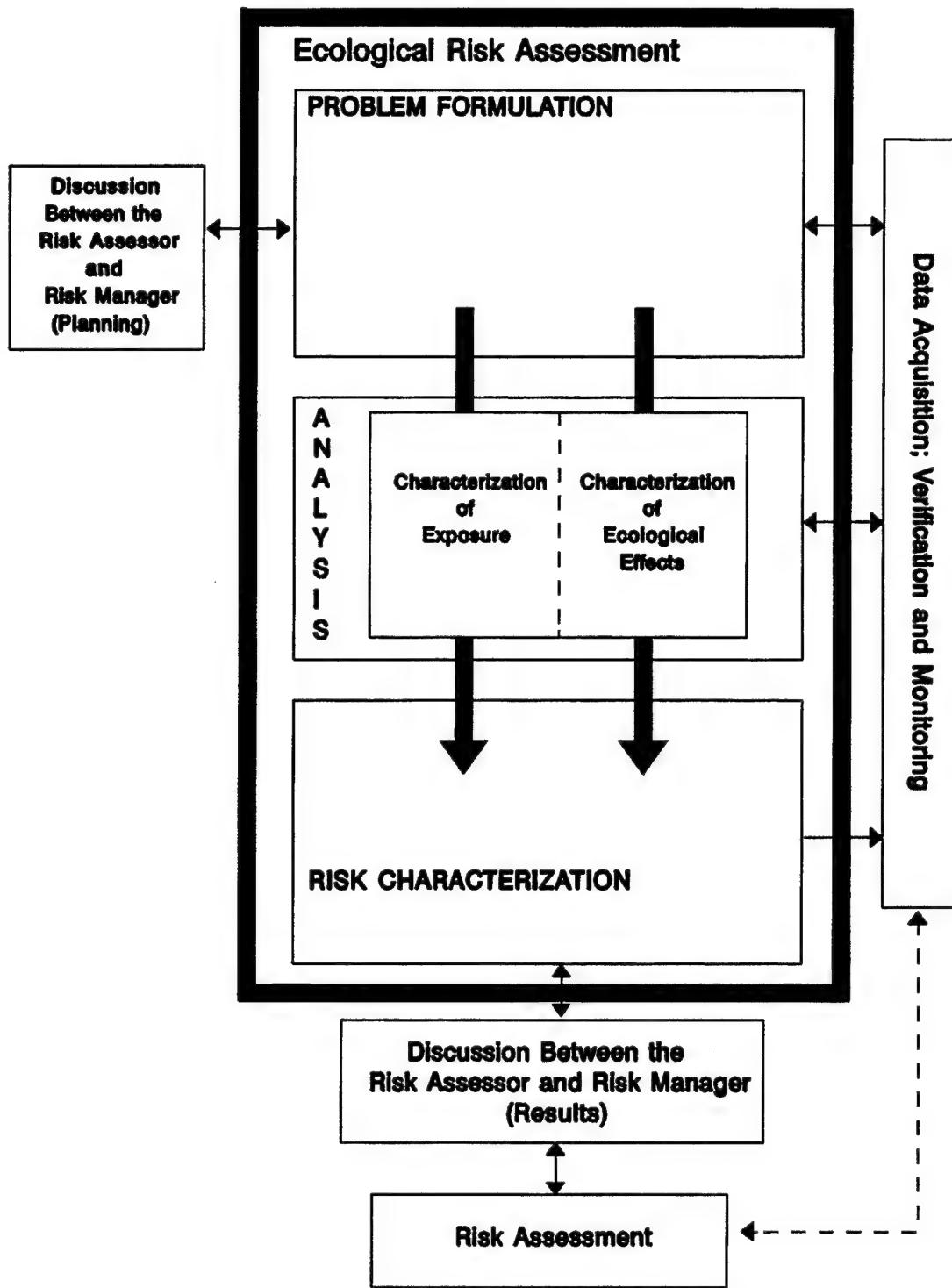
### Intended Audience

The use of ERAs is a relatively new practice in the arena of environmental resource or risk management. The majority of ERAs are used by risk managers who are in the process of reviewing damage to the environment caused by some previous activity for the purposes of assessing the amount of remedial actions that are required. This information may also be used as environmental documentation by program managers at testing and training sites, or by a risk manager to have the site placed on a priority list for special cleanup funding, like an EPA superfund. Program managers in the Base Realignment and Closure (BRAC), and risk managers from regulating agencies, EPA or state and local agencies, are familiar with ERAs. This ERA was funded by the Joint Projects Office (JPO) and written for program managers who maybe less familiar with an ERA, it will therefore contain more narration throughout the document. It is also intended as a predictive assessment. A predictive assessment is designed to help research, development and environmental program managers make decisions about exercise siting, type or magnitude. These decisions may prevent inappropriate testing that may necessitate a costly cleanup or remedial action down the road. The use of predictive ERAs will hopefully prevent the kinds of environmental contamination that has occurred historically from a lack of regard for the environmental consequences our activities may cause.

An ERA can help identify environmental problems, establish priorities, and provide a scientific basis for regulatory actions. The process can identify existing risks or forecast the potential risk of stressors not yet present in the environment. An ERA can also help program or risk managers decide whether or not the anticipated test or training site is appropriate for the activity. The purpose of this assessment is to predict the likelihood of adverse effect from the dissemination of graphite flake obscurants. Ecological risk may be expressed in a variety of ways. While some ecological risk assessments may provide true probabilistic estimates of both adverse effects and exposure elements, others may be deterministic or even qualitative in nature. In these cases the likelihood of adverse effects is expressed through a semiquantitative or qualitative comparison of effects and exposure.

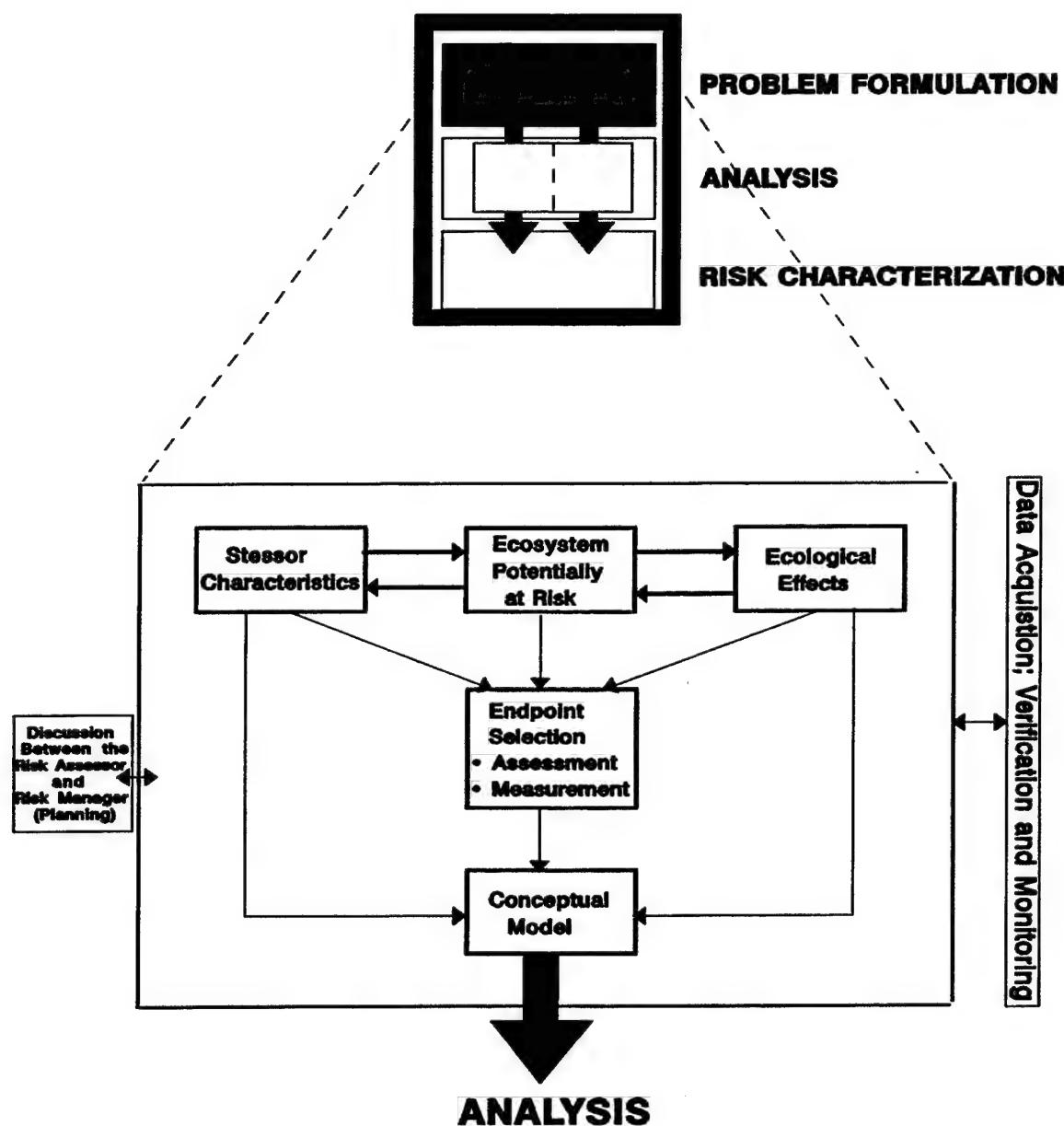
The Environmental Protection Agency (EPA) has established some guidelines on methodology for conducting an ERA. The EPA ERA framework document is used to conduct this ERA, a general format is has been suggested, figure 1 (EPA, 1992). The risk assessment process is based on three major elements: Problem formulation, analysis and risk characterization. Although characterization of exposure and characterization of ecological effects are most prominent during the analysis phase, aspects of both exposure and effects are considered during problem formulation, as illustrated by the arrows in the diagram. The arrows also flow to risk characterization, where the exposure and effects elements are integrated to estimate risk.

**Figure 1** A representation of the components of a Ecological Risk Assessment as recommended in the EPA's Framework for Ecological Risk Assessment document, February 1992.



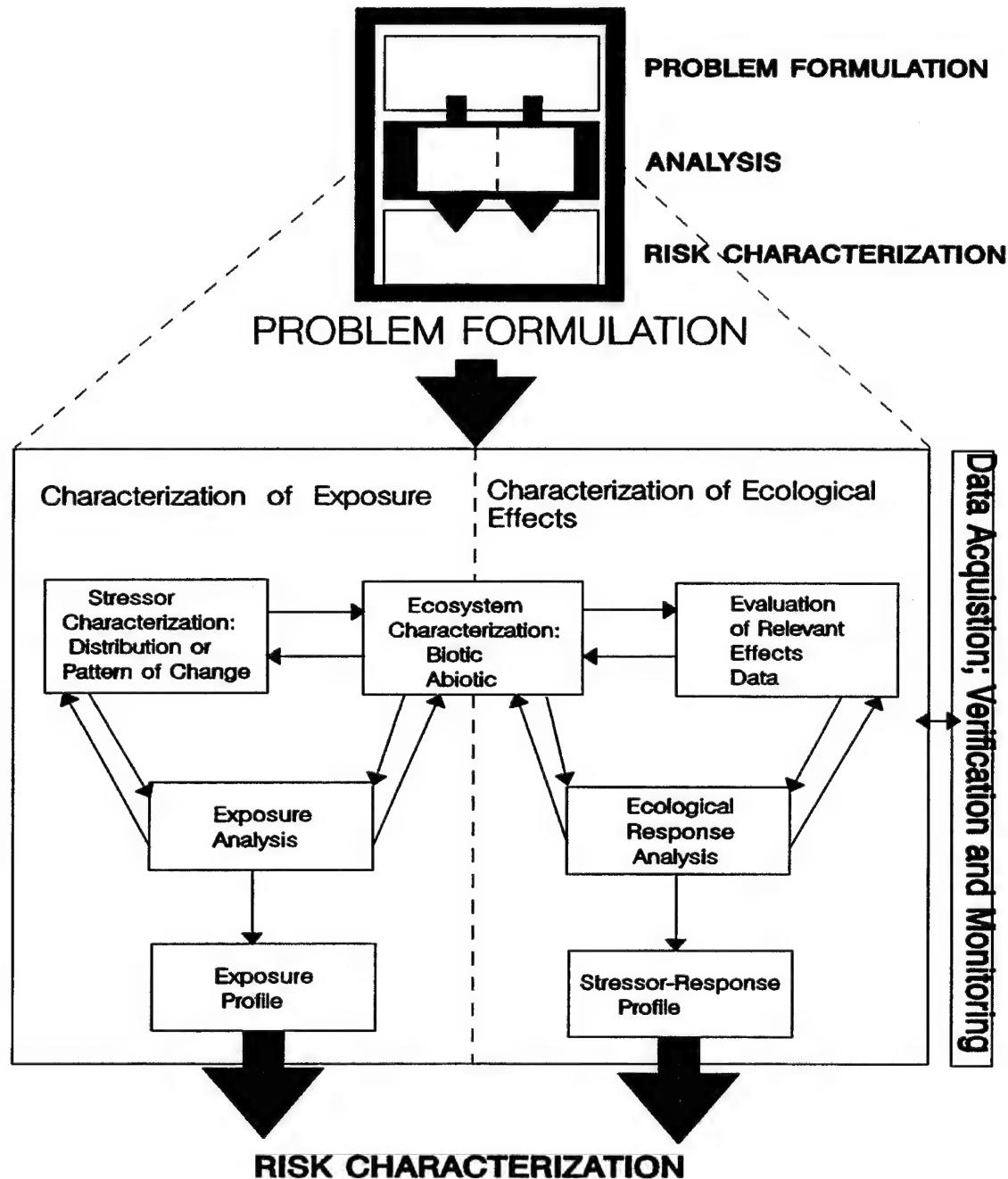
Problem formulation includes a preliminary characterization of exposure and effects, as well as examination of scientific data and data needs, policy and regulatory issues, and site-specific factors to define the feasibility, scope, and objectives for the ERA. The level of detail and the information that will be needed to complete the assessment are also determined. Problem formulation provides an early identification of key factors to be considered, which in turn will produce a more scientifically sound risk assessment.

**Figure 2** A representation of the components of the "Problem Formulation" section of an ERA recommended by the EPA's Framework for Ecological Risk Assessment document, 1992.



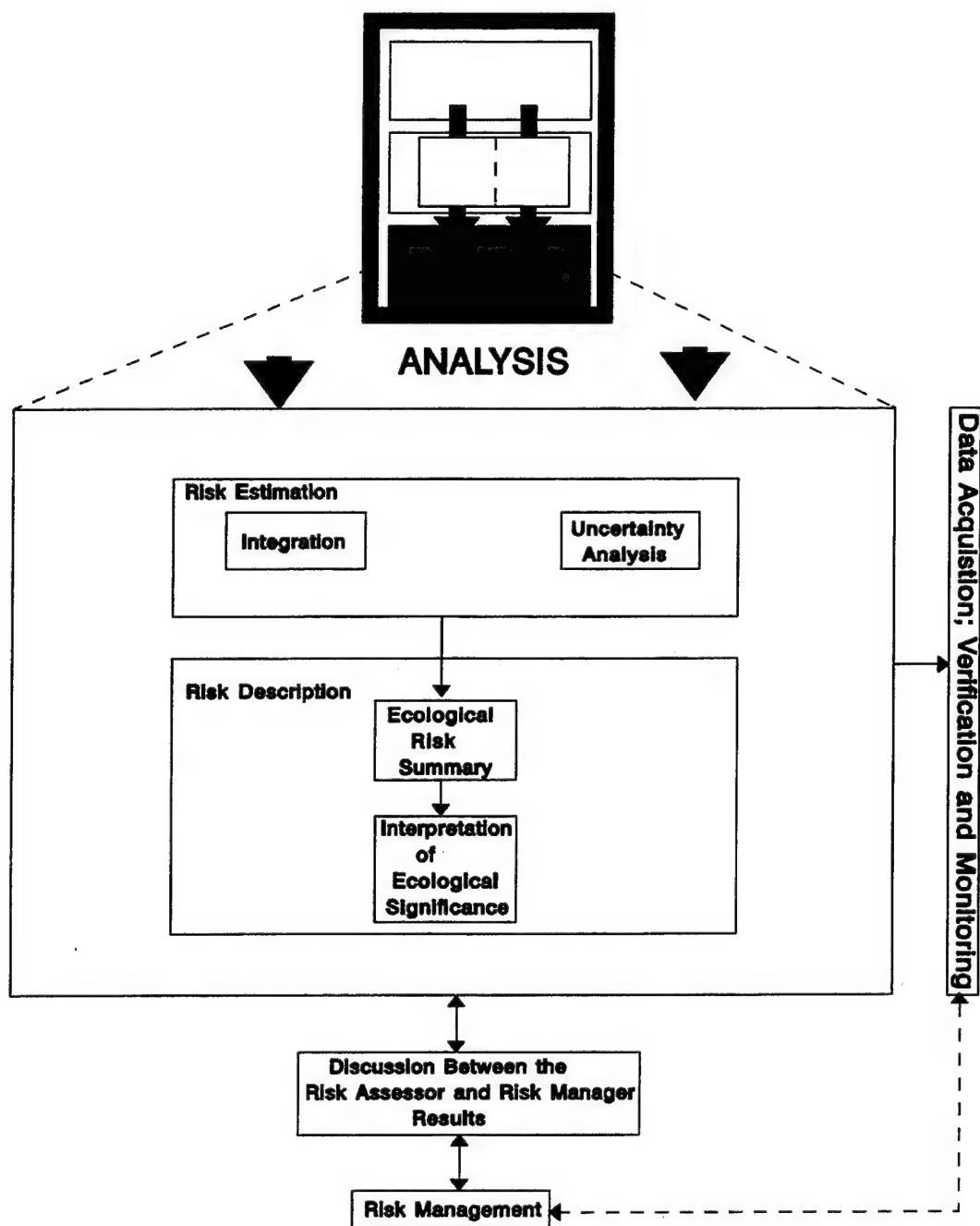
The analysis phase of the ERA consists of characterization of exposure and characterization of ecological effects sections. The purpose of characterization of exposure is to predict or measure the spacial and temporal distribution of a stressor and its co-occurrence or contact with the ecological components of concern. The purpose of the characterization of ecological effects is to identify and quantify the adverse effects elicited by a stressor and, to the extent possible, to evaluate cause-and-effect relationships.

**Figure 3** A representation of the "Analysis" section of an ERA from the EPA's Framework for Ecological Risk Assessment document, 1992.



Risk characterization uses the results of the exposure and ecological effects analysis to evaluate the likelihood of adverse ecological effects associated with exposure to a stressor. It includes a summary of the assumptions used, the scientific uncertainties, and the strengths and weaknesses of the analysis.

Figure 4 Representation of the Risk Characterization section of an ERA from the EPA's Framework for Ecological Risk Assessment document, 1992.



## 1.2

### Approach

This Predictive Ecological Risk Assessment will address the effect testing and training with graphite IR smoke may have on a terrestrial environment. This assessment is constructed as a screening level assessment or Tier I of a tiered assessment approach. The approach used in conducting an ERA is determined by site specific conditions, stressors involved, and the ecosystem potentially at risk. The intent of a tiered approach is to first investigate the nature and extent of effect a stressor may have had or the effect a anticipated stressor may have on the environment. The first tier assessment may uncover potential problems that may indicate the need for a more indepth and costly assessment. In the event that a more indepth ERA is required the Tier 1 assessment will have already identified problem areas such as data gaps, required literature, potential site surveys and environmental law and regulations that must be addressed. However, a Tier 1 ERA may indicate that there is little or no anticipated adverse environment effects from the previous or planned activity. If there is sufficient documentation to make scientifically sound risk characterization and risk management decision, no further work may be required.

This Tier 1 assessment will address the potential impact dissemination of a graphite infrared (IR) obscurant material may have on a terrestrial environment. In the problem formulation section we will address the proposed activity, dissemination of IR material, and the ecological components may be impacted by this activity. We will describe the ecological components used in this assessment and their role and importance in the environment. We will describe the IR material and the nature of its source as a possible environmental stressor and its application. This section will also include a review of environmental laws and regulations that may pertain to the activity of releasing graphite particulate into the environment.

In the characterization of exposure section we will present a model that estimates downwind concentration and deposition from a XM56 large area IR smoke generator. This model presents concentration and deposition data generated under several different meteorological test conditions at points several hundred meters and several kilometers down wind. Data collected under controlled conditions will be presented on the fate of IR material in the environment and its possible availability to environmental components.

In the Ecological Effect section, data demonstrating a cause/effect relationship between the stressor and the ecological components potentially at risk will be presented. The data presented will be from in-house toxicity studies conducted using indicator organisms and from data identified in the literature that demonstrated this cause/effect relationship.

Finally the Risk Characterization section will attempt to quantify the extent of the ecological risk associated with exposure to the stressor. The estimated risks are

discussed by considering the types and magnitudes of effects anticipated, the spatial and temporal extent of the effects, and recovery potential.

## 2. PROBLEM FORMULATION

Smokes are designed to hide a specific battlefield vehicle or large area troop and vehicle movements in areas where there would normally be a long line of sight, like large open range or meadow. Since smokes can carry large distances, perhaps up to 40 kilometers (Driver et al., 1993), their affect may reach beyond the anticipated field of utilization. It's therefore reasonable to believe that these materials may also be deposited on or find their way into neighboring agricultural areas.

Disseminated materials have the potential to deposit on and impact any environment downrange from the point of dissemination. For this assessment those areas of concern include ecosystems that are terrestrial in nature, thus potential deposition sites include plant surfaces and exposed soil. The deposited materials can potentially find their way into the soil, plant tissue, soil invertebrates and other soil biota. The impact a deposited material may have is also dependent on its reactivity and persistence in the environment. The toxicity and availability to local biota may change over time depending on the level of incorporation into the particular ecological system. We will examine the data available on the level of graphite incorporation and any effect graphite may have on a terrestrial environment.

### 2.1 Stressor Characteristics

Graphite is a soft-scale form of carbon that can be natural or synthetic in origin. Natural graphite is associated with quartz, iron oxide, mica, and granite impurities. Synthetic graphite is formed by heating petroleum coke, a binder (usually coal or tar pitch), and a petroleum based oil to facilitate extrusion of the particles. The characteristics of synthetic graphite depend on the composition of the mixture components, the temperature and length of processing, and the degree of orientation of the particles during extrusion (Driver et al., 1993).

"Synthetic" graphite is currently used by the U.S. military. There are currently only several producers of synthetic graphite worldwide. These producers distribute the synthetic graphite in a raw form to companies that mill the graphite into forms that are purchased for various applications including pigments, foundry facings, recarbonizing steel, lubricants and "lead" pencils. Two major suppliers of graphite used for military applications are Asbury Mills, trade name Micro 260, and Dixon Ticonderoga, trade name Dixon KS-2. The milling process employed by these companies produces a graphite particle with a "flake" or platelet geometry.

Graphite is typically used as a large area screening material generated by the modified MA-1A start cart or XM56. Typical dissemination rates for a fielded unit like the XM56 are 10 to 15 lbs/min. For large area screening and item testing scenarios the smoke output can be as high as 30 lb/min. The duration of a typical smoke test from a single large area screener like an XM56 is 30 minutes, however several generators are often run in sequence or even multiple generators at once. The frequency of dissemination is very much dependant on programmatic initiatives. For instance the annual "Smoke Week" testing at Eglin AFB occurs for approximately two weeks each year, but smaller tests are often conducted throughout the year. Frequency of smoke release can best be described as sporadic and episodic.

Graphite has been shown to be very stable when released into the environment (Dolezal et al., 1989). There is no observable breakdown of the material or incorporation into the soil. Stress associated with graphite would therefore be expected to be physical in nature. Accumulations of graphite on the soil surface when wetted may form a crust that may effect water infiltration or cause microclimatic changes. Models proposed by Driver et al. (1993) suggest that the highest concentration of graphite deposited to soil and foliar surfaces will occur within the first 100 meters downwind from the point of dissemination. Concentrations will decrease as distance from the source increases, however affected area will tend to increase as the graphite deposition spreads laterally.

## 2.2           **Ecosystem Potentially at Risk**

An ERA must begin with a conceptualization of the environment which will be considered to be subject to the effects. For assessments of individual developments, effluents, or chemical releases, the environment will be an actual place. For generic assessments of technologies or chemicals, it will be a reference environment which is representative of a site where a release would occur. Reference environments can be arrayed on a scale of abstraction. Values can be simply assigned to the parameters of the assessment models that are thought to be representative or even worst-case. This approach is appropriate for quickly screening chemicals. The appropriate degree of abstraction of the reference environment depends on the type of assessment to be conducted and the degree to which the characteristics of the likely release sites can be specified (Suter, 1993).

A principle consideration in environmental description are the boundaries placed on the environment and characterization of the entities and processes occurring within the boundaries. Boundaries may be defined by either (1) a regulatory or equivalent a priori definition or (2) properties of the assessment problem. An example of the first type would be that requirements of effluents meet some criterion at the edge of a zone of initial dilution. An example of the second type would be defining the boundaries in terms of the area within which the concentration of a chemical is higher than the concentration

at which a threshold for toxic effects occurs. Other commonly used approaches include the use of the bounds of applicability of a favored transport model, political boundaries, or a "reasonable" distance such as 1 km (Suter, 1993)

Since this assessment is constructed as a screening or Tier 1 assessment the environment under consideration here is not a specific location but a generic training/test facility. Smokes are designed to hide a specific battlefield vehicle, large area vehicle and troop movements or military installation in areas where there would normally be a long line of sight, like open range or grassland. Hence the ecological components described here will be limited to those of a relatively temperate, unforested rangeland. This level of abstraction is appropriate for a screening assessment of this type and for a material that has yet to demonstrate any terrestrial environmental toxicity at all. Since smokes can carry large distances, perhaps up to 40 kilometers (Driver et al., 1993), their affect may reach beyond the anticipated field of utilization. Since these materials can carry long distances we will assess their potential range of adverse ecological impact within the bounds of application of the Gaussian Plume Dispersion Model employed by Driver et al. (1993) for a 30 minute test, or 40 Kilometers.

There are many military test/training sites throughout the U.S. that have the potential to be cited for the application of large smoke screeners. The purpose of this Tier one assessment is to evaluate any effects to terrestrial environments, that is open range terrestrial environments. Terrestrial ecosystems are areas of potential impact at testing and training sites. Ecological components that will be assessed for potential impact are those that make-up the major components of a typical terrestrial ecosystem and receive direct deposition from environmental release of the IR smoke. These components include plants and plant species that can receive direct foliar deposition; the effect on plants from uptake of graphite through their root systems; the soil biota, including invertebrates and microbes; incorporation and effect on soil chemistry and physical characteristics.

### 2.3           **Ecological Effects**

Entry into the ecological risk assessment process may be triggered by either an observed ecological effect, such as visible damage to trees, identification of a stressor or activity of concern, or manufacturer of a new chemical (EPA, 1992). Currently there are no data that indicate graphite flake obscurants have any adverse effect on any terrestrial ecological components. Past military activities have been known to cause adverse effects, including the use of military battlefield smokes. Solid smoke materials do accumulate and concentrate in the environment. The U.S Army Corps of Engineers (1993), has measured elevated levels of IR smoke materials in soils taken at test area C-52A at Eglin Air force Base, FL. Eglin AFB which is the site of the annual "Smoke Week" testing for military countermeasure developmental items. This report does not site any specific environmental effects associated with the release of graphite IR materials. An Environmental Assessment (EA) conducted prior to release of Fog Oil and Graphite in

testing of the XM56 at Yuma Proving Ground, Yuma, Arizona (Driver et al., 1991) concluded that no significant impacts to air, water, and soil quality were anticipated. A finding of No Significant Impact was recommended by the EA.

### 2.3.1 Ecological Components

Green plants are the primary producers in the terrestrial ecosystem food chain. Their viability and productivity are direct indicators of the health of the ecosystem. Plants can indicate the presence of several types of stress including effects of temperature, photoperiodicity, moisture and nutrient availability, and toxins in the air, soil, and water. The effect of a contaminant on a terrestrial ecosystem can be most quickly observed by its effect from direct deposition to plant foliar surfaces. Wilting or burning of exposed surfaces can be very obvious for a stressor that has significant environmental toxicity. Effects of contaminant incorporation into the plant tissues from root uptake also indicate presence of stressor in the soil. For these reasons plants are used as indicators of environmental stress. This response should be measured as decreases in productivity and/or fecundity under laboratory and field conditions whenever possible. Measurements of ecological effect on plant indicator species used in an ERA should include an environmental concentration ( $EC_{50}$ ) that produces a 50 percent reduction in measured effect (eg. biomass production, fecundity). To be complete, an ERA for a terrestrial ecosystem should include the measure of plant response to the specific stressor.

Earthworms are key organisms in terrestrial ecological systems because of their role in maintaining the physical characteristics and processes of the soil, such as aeration, water permeability, and breakdown of organic matter. They increase the fertility of soil by increasing the availability of nutrients and are an important link in the food chain. Earthworms are also sensitive bioindicators of environmental stresses. Earthworms have been used by many authors to measure the toxicity of stressors in soils through bioassay and avoidance testing (Wentzel and Guelta, 1988). Toxicity measurements used in an ERA should include an  $LC_{50}$ , the concentration that causes 50 percent mortality in a standard 14-day microcosm test, and findings of lowest observable effect level (LOEL).

Soil microbial populations play a critical role in decomposing organic matter and the cycling of important nutrients (nitrogen, phosphorus, sulfur, and some trace metals). Microbial decomposition processes in the soil can also detoxify xenobiotic chemicals. Any physical or chemical perturbation to the soil system that impacts the microbial processes also impacts the soil system and vegetation. Measurements of soil microbial activity that should be included in scientifically sound ERAs include; soil dehydrogenase activity, a general measure of activity of the soil microbial activity; soil phosphatases, a broad group of enzymes that are important for the mineralization of phosphorus from organic matter; measurement of soil adenosine 5"-triphosphate (ATP) levels, a method for measurement of soil microbial biomass; total heterotrophic bacteria;

soil microbial diversity; and levels of soil nitrifying bacteria (Cataldo et al., 1990). Toxicity measurements of soil microbial activity used in an ERA should include an EC<sub>50</sub>, LC<sub>50</sub> and/or LOEL.

### 2.3.2 Data Requirements

Current research into the toxic effects of graphite on terrestrial ecosystem components is limited to studies conducted by the military or its contractors. There has been no reported adverse effect observed due to graphite smokes deposited to military test areas. Laboratory studies have been conducted on the effect of graphite in soil to earthworms and several plant species with no significant adverse effects. These findings are reported further in the analysis section of this assessment. A single study identified to date on material penetration into the soil showed no significant penetration. Data is lacking in the areas of effect on soil microbial activity, effect of foliar deposition and demonstrated effect to any terrestrial wildlife. There is evidence presented that graphite does not breakdown or become incorporated into soil chemistry. Studies to complete the data necessary to completely evaluate any effect from graphite smokes released into the environment are encouraged.

### 2.4 Endpoint Selection

Any ERA must have defined endpoints. There are two types of endpoints used in ERAs, assessment endpoints and measurement endpoints. An assessment endpoint is a formal expression of the environmental values to be protected, they usually refer to characteristics of populations or ecosystems on large scales, eg. forest or crop production in a geographical area or populations of specific species in a given area. The endpoint selected may vary for each site and its selection is based on a predetermined requirement for the site. Endpoint selection is normally driven by the site's intended end use and the resident or even transient populations or single species using the site. It is often difficult to quantitatively measure these changes to an assessment endpoint on such a large geographical area in the field. For screening level or Tier 1 assessments the data often used is the data available from toxicity tests using indicator species. The indicator species represents a cross over point between the large production of a population or ecosystem to the toxicity data collected in a small scale, controlled laboratory or field research project.

The measurement endpoints are the toxicologist's or field biologist's input into the assessment. The measurement endpoint is a formal, usually quantitative, expression of the results of toxicity testing of an indicator species. They are normally expressed in numbers such as a 96-hour LC<sub>50</sub>, the concentration found to kill 50 percent of the individual organisms over a 96 hour test period. Additional information may be expressed in the form of a concentration response curve where stressor effect/response can be indicated for various stressor concentrations (eg. LD, EC, or LC<sub>1.99</sub>) Measurements

used may also be obtained by environmental sampling and laboratory testing. (Suter,1993)

For site specific "Umbrella" ERAs and Tier 2 or 3 ERAs the indicator species employed may be those actually present at the site. For a screening level or Tier 1 assessment such as this, the data employed is that available from previous toxicity testing with more generic indicator species and species representative from specific sites identified through literature investigations and previous in-house toxicity testing. In addition to the species of organism used as an indicator, the medium used for testing, the soil the organisms are tested in, also come from previously available toxicity studies.

Because this is a Tier 1 level assessment and intended for broad use, and is not representative of a specific site, the assessment endpoints are also rather non-specific. Any application of an ERA to a specific site should include more site specific assessment endpoints that are normally specified by the site's risk managers. The assessment endpoints for measuring the environmental health and viability for this predictive assessment to a terrestrial ecosystem are; (1) no loss of production in select plant species; (2) no decrease in the viability of selected soil invertebrate and soil microbes; (3) no avoidance and/or loss of habitat of soil invertebrates.

Measurement endpoints employed will be LC<sub>10</sub>, LD<sub>10</sub>, No Observable Effect Level (NOEL), or Lowest Observable Effect Level (LOEL) to; (1) plant production using plant indicator species in 14-day acute toxicity tests; (2) earthworm lethal and sublethal effects in standard 14-day acute toxicity testing; (3) soil microbial dehydrogenase and phosphatase activity, soil microbial ATP levels (indicators of biomass), soil microbial diversity, and levels of soil nitrifying bacteria.

#### 2.4.1      Indicator Species

The selection of an indicator species used to represent a specific endpoint is often tied directly to the assessment site. For a specific site it is important to use a plant species that can be found on the site, that is, a characteristic species of the ecosystem potentially at risk. For example, forest or desert species may constitute the population at risk. In that case the species selected may be those of most value to man or of ecological dominance to the effected ecosystem.

Often the species used as an indicator may be more generic. When bioassays are conducted using a chemical of particular interest, the researcher may not have a specific application for the toxicity data generated. In those instances he may select an indicator species that is universally accepted for specific reasons. The plant species selected may be used as a food source or economically important cash crop. Their distribution, abundance and taxonomic representation may suggest a broad coverage in the plant kingdom. They may be sensitive to many toxic compounds and have been used to

some degree in previous bioassays. The use of an scientifically accepted species in various bioassays allows ranking of toxicity based on effect to a common species. The selected species may be compatible with environmental growth conditions or time constraints of the test method. The selected species may germinate easily and quickly or exhibit rapid and uniform growth. The seed may contain no natural inhibitors and require no special pretreatment or release mechanism (such as soaking, chilling, light or scarification) (EPA, 1982).

In the Environmental Effects Test Guidelines (1982) published by the EPA, a list of ten terrestrial plant species are recommended for the seed germination/root elongation, early seedling growth, and plant uptake tests. The species selected for plant bioassays by researchers are often taken from this list. Therefore, data on environmental effects often discovered via literature searches and reviews will be from studies conducted using these species. For Tier 1 and screening level ERAs the data used most often comes from these searches and reviews. Bioassays using site specific indicators are generated during more indepth site specific investigations. Toxicity data used in this ERA is of the type found through technical review and literature search. The limited data discovered to date report bioassay testing with graphite flake used the indicator species; (1) Zea mays (corn) a monocot from the EPA's listing of sensitive monocotyledons and; (2) Cucumis sativus (cucumber) from the EPA's list of sensitive dicotyledons. We have found that these species were used by other researchers to indicate toxicity to other smoke munitions, and that data can be easily compared to other findings. Two tree species Robinia pseudoacacia L. (black locust) and Acer rubrum (red maple), not as widely used as indicator species, were used in direct foliar deposition studies using graphite flake material by Sadusky (1991).

Data found in literature reviews of graphite effects on soil invertebrates use the earthworm indicator species Eisenia foetida. Eisenia foetida is a species that is widespread throughout the U.S. and is commonly used by researchers as indicators of toxic environmental effects. Since earthworms are constantly in contact with the soil, soil solution, and soil air spaces, they are a good indicator of biological stress. Data retrieved on effects of graphite in soil and other military smokes in soil have this species of earthworm in common.

In addition to the indicator species, the media in which environmental toxicity testing is conducted must be considered. The materials selected are subjected to the same type of criteria as a living indicator species. Often the medium, soil for example, has site specific application but can represent a widely dispersed soil type. For more generic applications, scientists often use an artificial soil that represents a standard test medium that can be widely employed in various assessments or evaluations and that produces data that is directly comparable. Thus allows the rating of a stressors toxic effect under standardized testing conditions. Descriptions of media identified from studies which investigated the toxicity of graphite are as follows:

- Sassafras sandy loam. A soil collected from M-field, a test area at Edgewood Research Development and Engineering Center, APG. MD. Described as a slightly acidic sandy loam (fine-loamy, siliceous, mesic Typic Hapludult) with low organic matter (OM) and low cation exchange capacity (CEC).

The Sassafras series consist of deep, well-drained, gently sloping to steep soils dominantly on undulating uplands, and some short steeper slopes of the coastal Plain. These soils formed on old marine deposits of sandy sediment containing moderate amounts of silt and clay. The soil used in testing from Aberdeen Proving Ground is further described as Sassafras sandy loam, 2 to 5 percent slopes, moderately eroded. This soil has a profile similar to the general series description, but the surface, or plow layer contains more sand, generally a little less clay, and less silt than does the plow layer of Sassafras loam. This soil is well suited to nearly all commonly grown crops. Native vegetation is mixed hardwoods, mainly oaks, with Virginia pine invading in places.

- Joppa sandy loam. A soil collected from an area near Winters Run stream in Edgewood MD. Described as a slightly acidic sandy loam (loamy-skeletal, siliceous, mesic typic Hapludult) with high OM and relatively high CEC.

The Joppa series consists of deep, well-drained to excessively drained, gently sloping to steep gravelly soils on the Coastal Plain. These soils formed in thick deposits of sandy and gravelly sediment that contain small amounts of silt and clay. They are generally in hilly areas in the higher parts of the Coastal Plain, close to the juncture with the Piedmont Plateau. The native vegetation is drought resistant hardwoods, mostly oaks, and some Virginia Pine. The soil used in soil fate testing described in this ERA is further described as Joppa gravelly sandy loam, 2 to 5 percent slopes. The soil is cultivatable, the plow layer is grayish brown or dark grayish brown. In areas where the slope is less than 2 percent the subsoil is red instead of brown. The low water capacity of this soil has more effect on its use and management in farming than the slight hazard of erosion. The soil is better suited to truck crops or early planted crops than to other crops. Joppa soils are easy to work, but pebbles are abrasive to farm implements.

- Artificial soil. A mixture of 10% sphagnum peat, 20% kaolinite clay, 69% fine sand, and 1.0% calcium carbonate. This mixture is often used by researchers to represent a generic soil that allows easy comparison of data from soil biota toxicity testing.

#### 2.4.2           **Conceptual Model**

The conceptual model is a hypothesis of what the stressor may be, how and to what extent it enters the environment in question, and speculation on routes of exposure and how environmental stress will be represented. ERAs that are constructed to assess pre-existing contamination to a specific area often speculate on the origination of the

environmental stressor. For this predictive assessment the source of the described stressor is known. Sources for graphite particulate releases are testing or training exercises using a large area smoke screener/disseminator mounted on some type of wheeled or tracked tactical vehicle. Graphite particles disseminated into the air can travel many kilometers before all the material settles to the ground or other surfaces. Higher concentrations of material will be observed near the generator with airborne concentrations and surface deposition decreasing with distance traveled away from the source. Any effect on ecological systems is expected to occur from direct deposition to surfaces or from movement of the material into a media like soil or groundwater, etc. Any effect on the environment that the stressor may have should be indicated by biological components within the area of graphite deposition. Plants may receive direct contact by deposition to leaf surfaces or indirect exposure by root uptake. Stress in plants may be indicated by changes in biomass production, seed or flower formation, and lack of or reduced seed germination. Animals in the soil may be also be effected from direct deposition or translocation downward into the soil. Indications of stress may be measured by monitoring the activity of soil microbes or invertebrates. Stress in soil invertebrates may be measured by loss of body mass, or avoidance of the affected area. Soil microbe stress may be indicated in a number of ways like changes in microbial diversity, total population, soil dehydrogenase activity, and respiration rate.

For a site specific ERA, measurements of these indicators may be made at the site or in lab studies using site specific biota. For this Tier 1 assessment we will rely on the indicator species already mentioned to predict possible effects at sites of similar environmental conditions. That is an environment loosely described as a temperate grassland or previously cleared natural forest area.

#### 2.4.3           **Environmental Toxicity Laws and Regulations**

Air Quality No national emission standard for hazardous air pollutants (NESHAPS) exist or are proposed for graphite (40 CFR 61). The new Clean Air Act Amendments of 1990 do not identify graphite as a specifically regulated pollutant. The Clean Air Act regulations have set National Ambient Air Quality Standards (NAAQS) for particulate matter less than 10  $\mu\text{m}$  in diameter (40 CFR 50) at 150  $\mu\text{g}/\text{m}^3$  for a 24 hour average concentration, and an annual geometric mean of 50  $\mu\text{g}/\text{m}^3$ . States must have plans to maintain these standards. The severity of local regulations will largely depend on whether or not the state is in compliance with the Federal Standard. State regulations must be consulted to determine allowable rates of dissemination and compliance monitoring methods. The initial concentrations and dissipation of graphite flake aerosols are discussed in the characterization of exposure section of this ERA and can be used to estimate potential compliance with NAAQS and local regulations (Driver et al., 1993).

Water Quality No point discharge of pollutants to waters of the United States, as defined by the Clean Water Act, would be expected to occur due to testing and

demonstrating of the graphite flakes. Therefore, a national pollutant discharge elimination system (NPDES) permit would not be required (40 CFR 122). The final NPDES permit regulation for storm water (55 FR 47990, November 16, 1990) also does not appear to be applicable to graphite flakes (Driver et al., 1993).

Because the flakes will be tested at a military installation having very large controlled land areas, it is not anticipated that the flakes will impact a community water supply system (40 CFR 141). Therefore, the safe Drinking Water Act's National Primary Drinking Water Regulations may not apply for most sites and releases. Consideration by specific site is recommended. Underground injection of liquids will not occur; therefore, an underground injection control permit is not required.

Hazardous Substance and Wastes Carbon is neither a listed hazardous waste under the Resource Conservation and Recovery Act (RCRA) or a hazardous substance under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

The U.S. Environmental Protection Agency (EPA) published on March 19, 1990, a toxicity characteristic leaching procedure (TCLP) final rule (55FR 11798-11877). This rule replaced the extraction procedure toxicity test for use in determining whether a waste stream exhibits the toxicity characteristic, added 25 organic compounds to a list of toxic constituents, and set regulatory levels based on health-based concentration limits. Carbon is not a TCLP listed constituent (Driver et al., 1993).

Emergency Planning and Community Right to Know Act (1986) provisions are not applicable to carbon.

Transportation Graphite flake is not considered a flammable or combustible material under the Hazardous Materials transportation Act (HMTA). Title C of the act addresses Class A explosives. If Class A explosives were to be used to disseminate flakes the transport of the pyrotechnic devices are subject to Class A explosives transportation regulations (49 CFR 173.53-173.87) (Driver et al., 1993).

Toxic Substances The Toxic Substance Control Act (TSCA) regulates the production, use, distribution, and disposal of chemical substances. This regulation is applicable to manufacturers and processors who must test certain substances to determine whether they represent an unreasonable risk to health or the environment. The TSCA is not applicable in this situation and does not include carbon as a toxic substance.

State Regulations State regulation may differ from federal regulations. Therefore, state regulations should be consulted in locations where activities occur that involve graphite flakes.

### **3. ANALYSIS**

#### **3.1 Characterization of Exposure**

##### **3.1.1 Stressor Characterization**

Graphite is a soft-scale form of carbon that can be natural or synthetic in origin. Natural graphite is associated with quartz, iron oxide, mica, and granite impairers. Synthetic graphite is formed by heating petroleum coke, a binder (usually coal or tar pitch), and a petroleum based oil to facilitate extrusion of the particles. The characteristics of synthetic graphite depend on the composition of the mixture components, the temperature and length of processing, and the degree of orientation of the particles during extrusion (Driver et al., 1993).

Because of its high purity and relative inertness, synthetic graphite is currently used by the U.S. military. There are currently only several producers of synthetic graphite worldwide. These producers distribute the synthetic graphite in a raw form to companies that mill the graphite into forms that are purchased for various applications including pigments, foundry facings, recarbonizing steel, lubricants and "lead" pencils. Two major suppliers of graphite used for military applications are Asbury Mills, trade name Micro 260, and Dixon Ticonderoga, trade name Dixon KS-2. The milling process employed by these companies produces a graphite particle with a "flake" or platelet geometry.

The flake geometry has the desired ability of relative efficiency at attenuating light in the Infrared (IR) wavelength, the wavelength used by sophisticated target acquisition systems. Its large surface/volume ratio and low settling velocity make flakes an obvious choice over materials with a spherical geometry. Descriptions of individual flakes include measurements of its major and minor dimensions. That is major being the face of the platelet and minor the thickness of the platelet. The milling process does not produce flakes of specific geometry in that, like a snow flake, they are beyond exacting description. Typically single flakes employed have a major dimension of 5.0 - 10.0  $\mu\text{m}$  and minor dimension of 0.1-0.5  $\mu\text{m}$ .

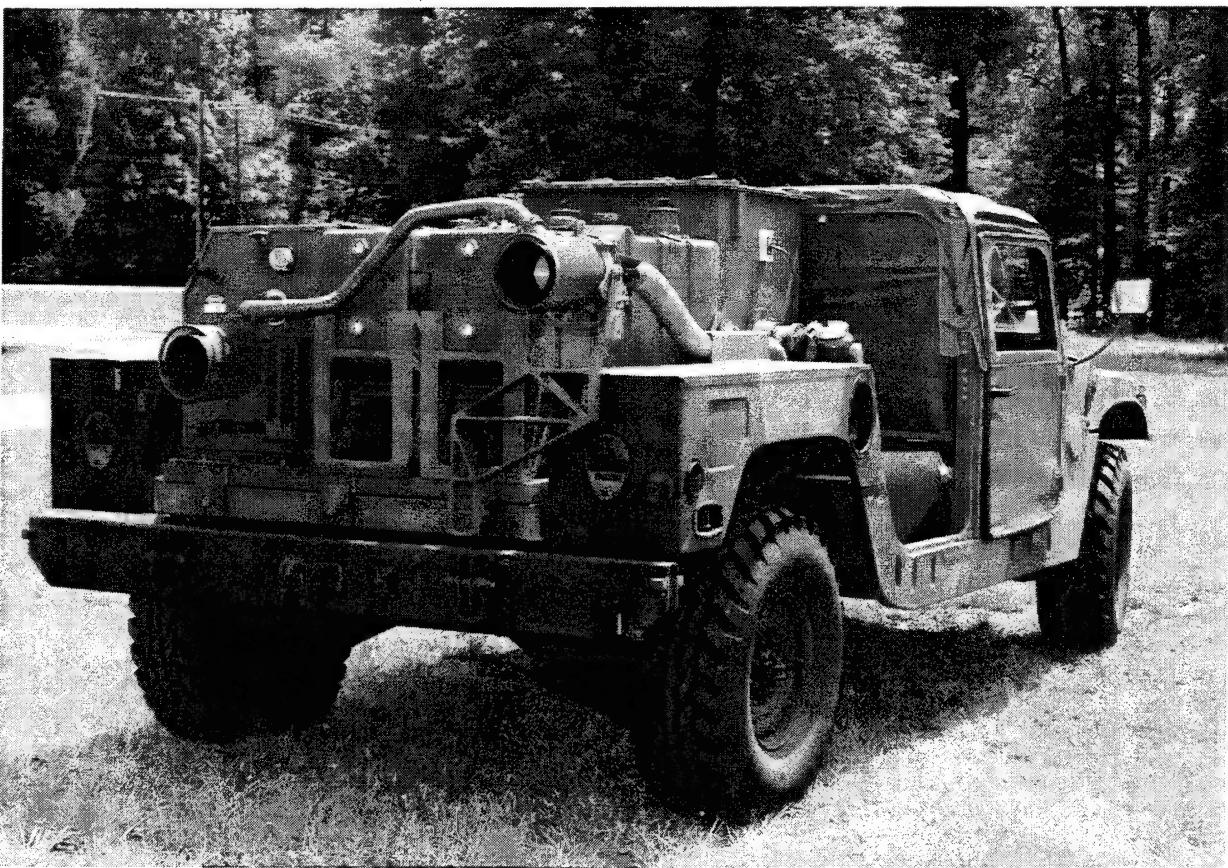
##### **3.1.2 Exposure Analysis**

Discussions of IR aerosol plumes must include measurement of plume concentrations in  $\text{mg}/\text{m}^3$ , that is mass of particles per unit volume, its extinction coefficient or alpha in  $\text{m}^2/\text{g}^{-1}$ , that is extinction per gram of material. Characterization of the average or mean size of the particles within the aerosol plume are expressed as an aerodynamic diameter. The aerodynamic diameter ( $D_a$ ) of a flake is the diameter of a unit density sphere that settles with the same velocity as the flake. The measurement of the mean particle size of the flake aerosol plume is expressed as Aerodynamic Mass Median

Diameter (AMMAD). That is the aerodynamic median diameter of the distribution measured on a mass basis as opposed to count or population basis. The spread of the distribution is expressed as Geometric Standard Deviation (GSD). Typical aerosol generated as IR smokes have an AMMAD of 2.5-3.5  $\mu\text{m}$  and GSD of approx. 2.5. Characterizations of flake aerosol particle size from the XM56 have been examined in depth by Guelta et al. (1993a,b).

Graphite is typically used as a large area screening material generated by the modified MA-1A start cart, XM56, or SG18. Typical dissemination rates for a fielded unit like the XM56 are 10 to 15 lbs/min. For large area screening and item testing scenarios output can be as high as 30 lb/min.

Figure 5 The XM56 is a Highly Mobile Multipurpose Utility Vehicle (HMMUV) Mounted System that can Disseminate Graphite (IR Obscurant) and Fog Oil (Visual Obscurant). The XM56 disseminates 10 lbs/min graphite for up to 30 minutes for a single run.



Ideally smoke testing conditions for obscurant materials fall into a rather narrow range of operation. Most smoke dissemination testing is done under relatively low wind conditions and moderate amounts of atmospheric turbulence to facilitate effective cloud formation and downwind dispersion. Under milder wind conditions and low turbulence, surface deposition in the area of dissemination can be expected to be much greater than under more energetic conditions.

### 3.1.3      **Exposure Profile**

Several models are available for predicting deposition and airborne concentrations. Most common smoke dispersion models currently rely upon Gaussian distribution and statistics. For this study we will use a Gaussian plume dispersion model employed by Driver et al. (1993) to predict downwind aerial concentration and ground deposition of graphite material disseminated from a XM56 for a normal 30 minute and 300 minute tests for distances beyond several hundred meters downwind. Several site conditions accounted for in the model include, wind velocity, and turbulence, degree of insolation, height of ejector discharge, particle settling velocity and other parameters. Driver developed data for 6 scenarios that would cover the range of possible field conditions resulting in the possible minimis and maximus material deposition. Plume disseminations used to determine graphite deposition for cases 1 through 6 are listed in Table 1. Parameters that were varied include the atmospheric stability category (ASC), plume dispersion height (H), mean wind velocity (u), and material deposition velocity (Vd).

Pasquill-type atmospheric stability categories (ASC) are described as: A) extremely unstable, B) moderately unstable, C) slightly unstable, D) neutral, E) slightly stable, and F) moderately stable. Each of these categories are also influenced by wind speed and insolation, see Driver (1993).

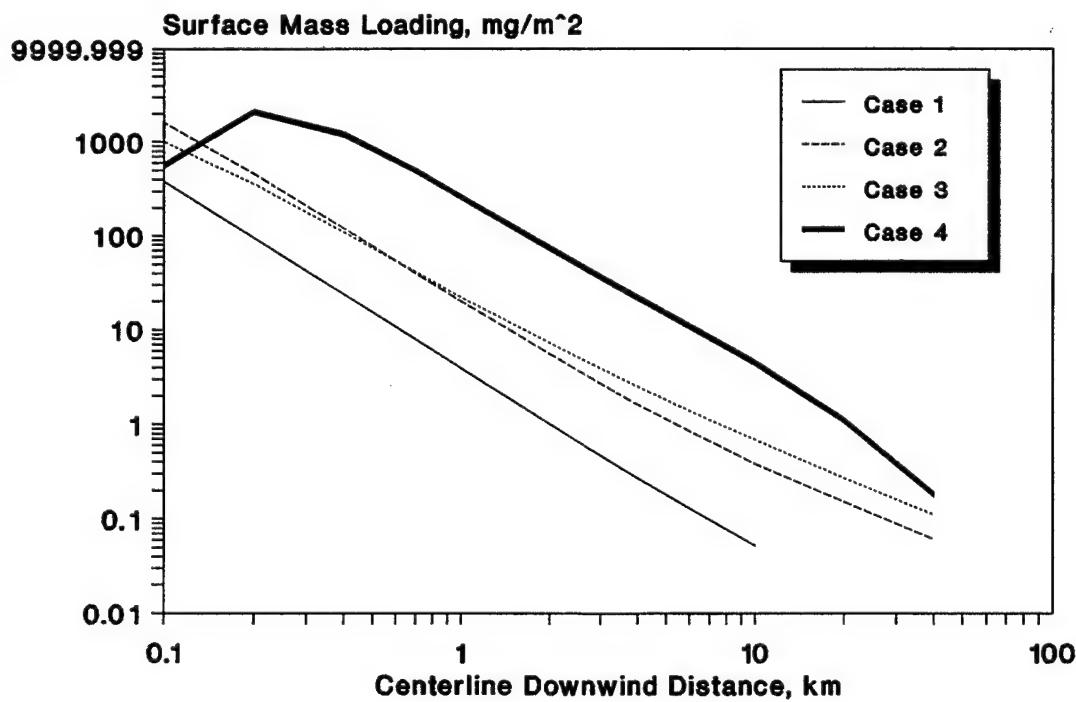
Cases 2 and 3 are thought to represent the most typical parameters for test conditions. Case 1 represents extremely unstable atmospheric conditions during which tactical release of graphite flake aerosols may be least effective because of rapid plume dispersion but during which time the lowest environmental risk may be expected due to reduced deposition levels. Case 4 represents moderately stable conditions that are not common at most sites, but it represents a worst-case condition along the mean wind vector. Cases 5 and 6 were selected to demonstrate the predicted impact of wind speed, plume height, and generation time, respectively.

**Table 1** Test Case Parameters for Estimating Graphite Flake Aerosol Plume Dispersal in the Atmosphere and Deposition to Ground Surfaces.

Case	Parameter	Q <sub>p</sub> (g/s)	H (m)	u (m/s)	ASC	V <sub>d</sub> (cm/s)	t (min)
1	ASC	76	5	2	A	0.8	30
2	ASC	76	5	2	C	0.8	30
3	ASC	76	5	5	D	0.8	30
4	ASC	76	5	2	F	0.8	30
5	u	76	5	5	C	0.8	30
6	t	76	5	2	C	0.8	300

Figure 6 represents surface deposition estimates for Cases 1 through 4 above. Deposition estimates for Case 6 can be expected to be a factor of 10 higher than Case 2 due to a longer dissemination time. Estimates are for centerline concentrations, deposition can be expected to be lower away from the centerline. In predicting the concentration and deposition of the graphite plume the assumption is made that wind velocity and vector are constant. These parameters of course are constantly varying under field conditions so actual deposition numbers seen in the field may be lower.

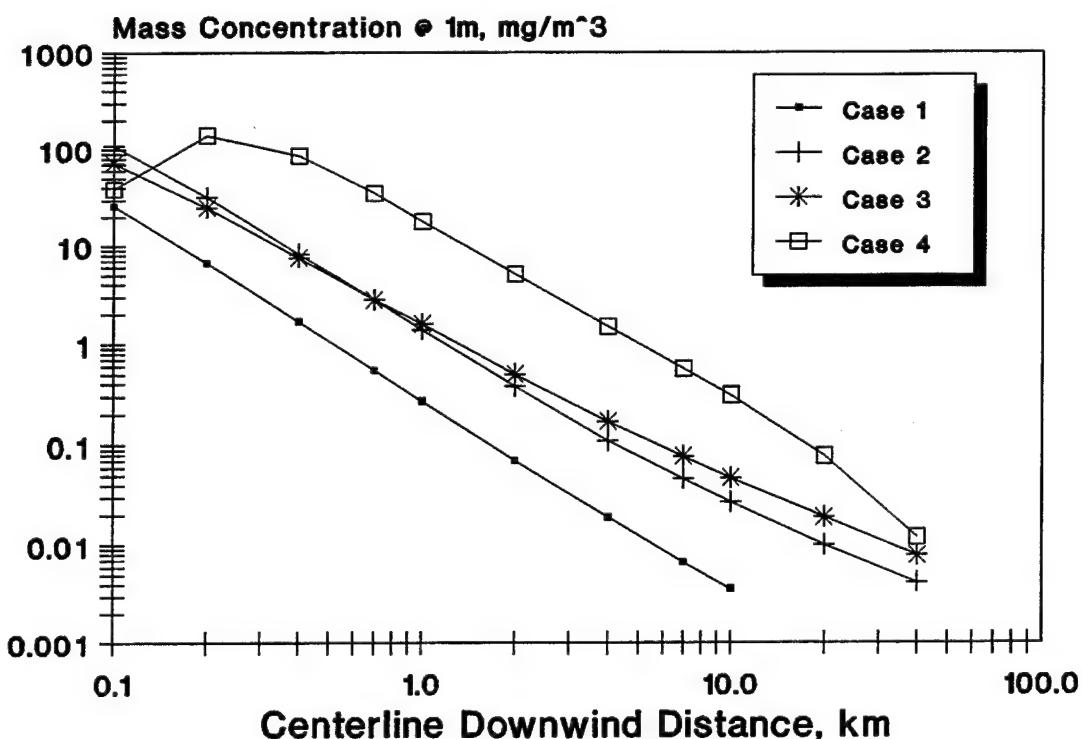
**Figure 6.** Estimated Graphite Flake Deposition. Mass loading was determined using a modified Gaussian plume deposition model. Cases 1 through 4 are shown.



This model, while useful for this study, may not be completely applicable for specific sites with well defined conditions. Other models available include the "Industrial Source Complex Dispersion Model" and "Real-Time Volume Source Dispersion Model". The model employed for specific sites should be evaluated on a case-by-case basis.

Figure 7 represents the expected graphite concentration at a point 1 meter above the ground. While foliar and ground surface deposition are associated with stressor dosage to plant and soil components of the terrestrial environment, airborne concentration can also have negative impact. A portion of the impact to wildlife is through direct inhalation of smoke particles. Figure four represents plume concentration at 1 meter above ground. While our abstract environment at risk has been described as a open field or meadow birds and insects could be affected by the airborne particulate.

Figure 7. Graphite Mass Concentration at 1 Meter above ground. Estimated using a Modified Gaussian Plume Deposition Model. Cases 1 through 4 are shown



### 3.1.4

#### Fate of Graphite in Soil

The fate of materials in soils typically has great bearing on its final availability to soil microbial activity, soil invertebrates and plants. There are relatively large amounts of data on fate of other smoke materials in soils. To date few studies have been done on the fate of graphite in soils. Dolezal et al. (1989) examined the fate of graphite in soil cores over a two year period. Graphite was placed on the soil surface and allowed to weather naturally in an often varying Maryland environment for two years. Soils used for soil column testing include a Sassafras sandy loam collected from M-field area of Aberdeen Proving Ground MD and a Joppa sandy loam collected near Winters Run stream in Edgewood MD.

- Sassafras sandy loam. A soil collected from M-field a test area at Edgewood Research Development and Engineering Center, APG. MD. Described as a slightly acidic sandy loam with low organic matter (OM) and low cation exchange capacity (CEC).

The Sassafras series consist of deep, well-drained, gently sloping to steep soils dominantly on undulating uplands, and some short steeper slopes of the coastal Plain. These soils formed on old marine deposits of sandy sediment containing moderate amounts of silt and clay. The soil used in testing from Aberdeen Proving Ground is further described as Sassafras sandy loam, 2 to 5 percent slopes, moderately eroded. This soil has a profile similar to the general series description, but the surface, or plow layer contains more sand, generally a little less clay, and less silt than does the plow layer of Sassafras loam. This soil is well suited to nearly all commonly grown crops. Native vegetation is mixed hardwoods, mainly oaks with Virginia pine invading in places.

- Joppa sandy loam. A soil collected from an area near Winters Run stream in Edgewood MD. Described as a slightly acidic sandy-loam with high OM and relatively high CEC.

The Joppa series consists of deep, well-drained to excessively drained, gently sloping to steep gravelly soils on the Coastal Plain. These soils formed in thick deposits of sandy and gravelly sediment that contain small amounts of silt and clay. They are generally in hilly areas in the higher parts of the Coastal Plain, close to the juncture with the Piedmont Plateau. The native vegetation is drought resistant hardwoods, mostly oaks, and some Virginia Pine. The soil used in soil fate testing described in this ERA is further described as Joppa gravelly sandy loam, 2 to 5 percent slopes. The soil is cultivatable, the plow layer is grayish brown or dark grayish brown. In areas where the slope is less than 2 percent the subsoil is red instead of brown. The low water capacity of this soil has more effect on its use and management in farming than the slight hazard of erosion. The soil is better suited to truck crops or early planted crops than to other crops. Joppa soil are easy to work, but pebbles are abrasive to farm implements.

**Table 2.** Soil Parameters from Testing by Dolezal et al., 1988.

Soil	Texture	pH (units)	Mg	P2O5	K2O	B	Ca	CEC (meq)	Mn	NO3
"M" Field (MS)	loam	4.6	15	3	32	.1	40	3.6	6	3.5
Winters Run (WR)	loam	5.1	117	13	37	.4	640	8.3	80	13
<hr/>										
Soil		% Organic Matter		% sand		% silt		% clay		
"M" Field (MS)		3.5		32		50		18		
Winters Run (WR)		7.2		50		36		14		

Soil columns were removed from the test every 6 months and evaluated for vertical migration of graphite, and graphite chemical or physical breakdown. Vertical migration of the graphite was evaluated at depths of 0-2.5 cm, 2.5-5.0 cm and 5.0-10.0 cm. Over the span of two years some graphite material was observed in the 2.5-5.0 cm depth of the soil columns although this migration was not consistent with each 6 month observation. The migration to the 2.5 to 5.0 cm depth was observed in both soil types. Scanning Electron Microscope analysis of the flakes taken over time showed no physical or chemical breakdown of the material. The material did not fracture, split, pit or appear to breakdown in any way, thus appearing environmentally inert. Because the material is so inert and migration spotty the movement of the graphite into the soil could be due to heavy frost heave or water flow movement rather than soil chemical processes.

Anticipated soil penetration and resultant concentrations can be calculated based on a migration depth of 5.0 cm. Graphite concentrations in the soil could be a gradient from the surface to the anticipated 5.0 cm. For ease of presentation and calculation concentration will be assumed to be uniform to a depth of 5.0 cm. Surface deposition employed will be from the Gaussian Plume distribution model introduced earlier using Case 4, the conditions of highest anticipated spot concentration and deposition.

**Table 3 Calculated Graphite Air, Soil Surface Deposition and Soil Concentration  
Estimated Using the Gaussian Plume Distribution Model from Driver et. al.,(1992) Case 4.**

Distance Downwind (Km)	Dissemination Rate (lbs/min)	Concentration Air @ 1 meter (mg/m <sup>3</sup> )	Deposition to soil surface (mg/m <sup>2</sup> )	Soil concentration (ug/gm)
0.1	10	38.0	1200	19.2
1.0	10	9.4	300	4.8
5.0	10	0.5	15	0.24
10.0	10	0.15	4.5	0.072
40	10	6.1^-03	0.2	0.032

Soil concentration calculated using soil density of 1.25 gm/cc

Because the material is so inert and remains on the soil surface, resuspension of the material by wind may be a concern. Resuspension should not be a concern in high vegetation/high surface roughness areas. In areas with less vegetative cover of the soil surface resuspension of the material will occur.

#### **4. ANALYSIS: CHARACTERIZATION OF ECOLOGICAL EFFECTS**

##### **4.1 Terrestrial Effects**

Graphite flakes used as obscurants in training activities will be deposited on soil and vegetative surfaces in varying amounts. Although graphite has several impurities their combined weight is less than 1.0 percent and not expected to have significant impact. While many of the other smoke materials have been studied in some detail, there is little data on the effect of graphite. This is in part due to its relatively recent application in the area of battlefield obscurants and that toxicity studies done to date by the Army or its contractors have shown that ecological components of a terrestrial environment have demonstrated little or no adverse effects at levels above anticipated battlefield exposures. Also synthetic graphite is stable and pure enough that little decomposition or incorporation into soil or water chemical cycles is anticipated. It therefore receives little priority for continued funding for environmental toxicity research...and perhaps rightly so.

#### **4.2                  Effect on Soil Microbial Activity**

Effect of materials on soil microbial activity is a good indicator of stress to a terrestrial ecosystem. Investigators have measured the effects of other smoke materials on soil microbial activity. Data on the effects of graphite on soil microbial activity are lacking and may be a consideration for future graphite/environmental toxicity studies.

#### **4.3                  Soil Invertebrates**

Earthworms are a key organism in the soil community, because of their role in maintaining soil physical characteristics and processes such as aeration, water permeability, and breakdown of organic matter. Earthworms are a key indicator in assessing the effects of a toxin to terrestrial communities. Studies to examine the toxic effect of graphite in soil to the earthworm Eisenia foetida have indicated that graphite has no toxic effect in the concentrations studied.

Bowser et al. (1989) tested the effects of graphite in artificial soil at concentrations ranging from 500 ug/g to 10,000 ug/g. Results indicate no toxic or sublethal effects at any concentration tested. There are no other data available for toxicity of graphite in soil to earthworms.

#### **4.4                  Effect on Plants through Soil Amendment**

Bioassays using plants are a excellent indicator of a toxins possible effect on terrestrial ecosystems. Open dissemination of graphite flakes will cause deposition to exposed soil and plant surfaces. Data is limited on the effect of graphite on plants. Phillips and Wentsel (1990) found no significant effect of graphite-amended soil to corn (Zea mays) and cucumber (Cucumbus sativus L.) grown on a Joppa sandy-loam soil. No significant effect in plant shoot heights were found at soil concentrations of 500 to 10,000 ug/g.

#### **4.5                  Effect on Plants through Foliar Deposition**

The effect of a stressor deposited directly to plant surfaces is a good indicator of a stressors toxicity. Stress would be indicated by complete or partial defoliation, chlorosis or necrosis of exposed leaf surfaces, and any adverse effects to new plant growth. In testing using the XM56 large area screener, Sadusky (1990-91) exposed tree species Black locust and Red Maple, and cultivated crop species Zea mays and Cucumbus sativus to a graphite plume of the X56. No adverse effects from the graphite deposition were noted on surfaces receiving direct deposition or new plant growth.

#### 4.6

#### Effect on Wildlife

The possible avenues of effect of graphite to wildlife are through direct contact, consumption, and inhalation. To date we have found no data or evidence to support any adverse effect from direct contact with graphite to any wildlife species.

Consumption of graphite flake material while foraging is unlikely to cause any adverse effects to mammals or birds. Impact to wildlife from diminished food sources will probably be minimal because the area on which graphite flake deposits would be large enough to cause plant or invertebrate damage is relatively small to most foraging animals (Driver et al., 1993). To date we have found no data on effects of graphite from consumption.

Wildlife remaining within about 0.2 km to 4 km downwind of the test site during smoke generation periods may inhale potentially harmful levels of graphite. This assumes that wild animals have about the same sensitivity to air pollutants as humans and receive (on a body-weight basis) equivalent doses in the environment. However it has been shown that the volume of air breathed per minute per unit of body weight varies greatly among mammals. Generally, the smaller the animal, the more air per minute per gram is inhaled. Compared to humans, rabbits ventilate 3 times and small rodents ventilate 8 to 13 times greater volumes of air on a per body-weight basis. Larger animals such as moose and deer receive smaller doses than humans during inhalation exposures. Birds may be at even greater risk than presented in human Short Term Exposure Limit (STEL) because their respiratory rates are generally higher than mammals of comparable size. In addition, seasonal physiological changes, activities, and breathing-zone differences further complicate the extrapolation of human STEL to wild animals. Therefore, the STEL (10 mg/m<sup>3</sup>) for humans should be viewed as a relative estimate of the safe limit for wildlife in field situations (Driver et al., 1993)

The only inhalation data indicating potential harm to wildlife discovered to date is that of Thompson et al. (1986, 1988). For rats, single exposures up to 500 mg/m<sup>3</sup> of graphite flake caused only transient pulmonary damage. However, repeated graphite exposures to lower airborne concentrations (100 mg/m<sup>3</sup>) of graphite flake apparently overwhelmed the clearance mechanisms and pulmonary lesions developed in response to the retained flakes. It should be noted while stress from graphite exposure has been documented in rats, the high concentration of graphite used to cause noticeable effect is only observed in the graphite plume immediately after the point of dissemination, a position that mobile wildlife would be expected to vacate due to noise propagation and close proximity to human activity.

## **5. RISK CHARACTERIZATION**

Risk characterization is the final phase of risk assessment. During this phase the likelihood of adverse effects occurring as a result of exposure to stress are evaluated. Risk characterization has two major steps: risk estimation and risk description. The stressor-response profile from the analysis phase serve as input to risk estimation. The uncertainties identified during all phases of the risk assessment are analyzed and summarized. Supporting information in the form of a weight of evidence discussion is also presented during this step (EPA, 1992).

Risk description has two primary elements. The first is the ecological risk summary, which summarizes the results of the risk estimation and uncertainty analysis and assesses confidence in the risk estimation through a discussion of the weight of evidence. The second element is interpretation of ecological significance, which describes the magnitude of the identified risks to the assessment endpoint (EPA, 1992).

### **5.1 Risk Estimation**

To be a risk to any environmental components or assessment endpoints a stressor must be demonstrated to co-exist, be available to, or be in contact with the components of the environment at risk. We have described the environment at risk as a generic terrestrial environment consisting of grasslands or meadow. The components of the ecosystem at risk have also been described as green plants, soil invertebrates and various soil microbiota. When graphite obscurant material is disseminated during training or testing exercises two basic things happen to the disseminated material. First the plume is carried with the ambient wind currents. The plume expands as it mixes with the air and becomes less dense as it travels downwind. Second, as the plume moves material is lost or deposited to any surrounding stationary surfaces that the plume encounters. We of course are most interested with those surfaces that are or can affect local environmental surfaces, plants and animals.

The characterization of exposure section has presented modeled data for graphite plume concentrations and deposition rates for several wind conditions and atmospheric stability scenarios. This data is very useful in determining the availability of graphite material to the environmental components. According to Driver et al., (1993) under gentle wind and atmospheric mixing conditions, deposition to ground surfaces can be as high as  $1600 \text{ mg/m}^2$  at 100 meters from the source, decreasing to  $6.1^{-02} \text{ mg/m}^2$  40 kilometers downrange. Under higher wind speeds and less stable atmospheric mixing conditions, deposition levels downrange could be as low as  $3.8 \text{ mg/m}^2$  and  $5.2^{-02} \text{ mg/m}^2$ , 10 kilometers down range.

Graphite is a very stable material. Dolezal et al. (1988), reported no observable breakdown or reactivity of graphite material in soil columns over a period of

two years. The material does not undergo chemical or biological degradation, but breakage of the material may occur. If not mechanically incorporated into the soil surface by rainfall or plant debris, resuspension of the material may lessen the concentration of material on the soil surface. Since the material is so stable it is therefore available to interact with the ecological components if possible. To date there are no data to indicate that graphite flakes are able to migrate substantially below the soil surface, although Wentsel and Guelta (1986) concluded that brass material from brass flakes does migrate approximately 2 to 3 inches below the surface. Brass however has been shown to breakdown when exposed to the soil environment. Any interaction with graphite by plant root systems, invertebrates and soil microbiota would have to be assumed to occur only at the soil surface until data can show otherwise.

The stability of graphite may prove that it will be available to ecological components for extended periods of time. However, the material itself has not been shown to remain in the place where it was originally deposited. Unless the material is tied to some environmental component or to itself in sufficient quantity, resuspension of the material may be a factor in assessing final environmental concentrations. To date we have not discovered any data assessments of the fate of graphite flake material in any terrestrial environment.

### **5.1.1        Integration of Stressor-Response and Exposure Profiles**

The intention of stressor-response and exposure profiles in a predictive ERA are to assess the chances of environmental stress and predict the level of stress based on the exposure profiles from the characterization of exposure section of the ERA. Presently the stressor-response data available has yet to show any signs of stress to plant and animal indicator species. The testing conducted to date has not provided the toxicity information required to meet any quantifiable toxicity, even though graphite soil concentrations used were several orders of magnitude higher than anticipated from field testing. The measurement endpoints selected for this ERA are LC<sub>10</sub>, LD<sub>10</sub>, No Observable Effect Level (NOEL), or Lowest Observable Effect Level (LOEL) to: (1) plant production in 14 day acute toxicity testing; (2) earthworm standard 14-day acute toxicity testing; (3) soil microbial activities. For measurement endpoints 1 and 2 no observable effect level (NOEL) has been demonstrated at concentrations at least two orders of magnitude higher than those anticipated in field testing of the type described in this assessment. To date there are no data available from testing of soil microbial activities.

**Table 4** Summary of Predicted Downwind Soil Concentrations of Graphite Incorporated into the Soil to 5.0 Centimeters, and Summary of Soil Concentrations and Results from Earthworm and Plant Toxicity Testing.

Distance downwind	Soil conc.	Earthworm test soil conc.	Effect level	Plant test soil conc.	Effect level
0.1 Km	19.2 ug/g	10,000 ug/g	NOEL	2500 ug/g	NOEL
1.0 Km	4.8 ug/g	5,000 ug/g	NOEL	500 ug/g	NOEL
5.0 Km	0.24 ug/g	1,000 ug/g	NOEL	250 ug/g	NOEL
10.0 Km	0.072 ug/g	500 ug/g	NOEL		

To date, terrestrial toxicity data is only available from earthworm and plant production testing. These tests yielded very useful information on the relative toxicity of soil amended with graphite flakes. Currently there is no information that graphite material will migrate into the soil, causing exposures as high as those demonstrated in acute toxicity testing. Theoretically, in the event that the environment exposed to graphite flake deposition was plowed for farming, the soil amendment data would be useful in predicting stress to agricultural plants and earthworms provided graphite concentrations employed in the standard acute toxicity test were high enough to produce indications of stress.

To date there is little data on effect of graphite material deposited on foliar surfaces, fate of graphite in soil or the environment, effect of graphite deposited to the soil surface on soil invertebrates, or soil microbial activity. There are no data on the effects of graphite on wildlife, other than laboratory rats. We have yet to find any data showing effects of graphite on any other component of a terrestrial environment other than the two studies mentioned, Bowser et al., "Toxicity of Graphite Flakes in Soil To Earthworms", 1990, and Phillips and Wentsel, "The Effects of Graphite Flakes In Soil on Terrestrial Plants", 1990. The data that currently exist for toxicity of graphite indicate that graphite is not toxic enough to construct reasonable Stressor-Response profiles... that is, to date, no response other than NOEL can be reported.

### **5.1.2        Uncertainty Analysis**

The uncertainty analysis identifies and, to the extent possible, quantifies the uncertainty in problem formulation, analysis, and risk characterization. The uncertainties from each of these phases of the process are carried through as part of the total uncertainty in the risk assessment. The output from the uncertainty analysis is an evaluation of the impact of uncertainties on the overall assessment and, when feasible, a description of the ways in which uncertainty could be reduced (EPA, 1992).

The uncertainty associated with this assessment is in the limited amount of data available to date in the characterization of exposure and ecological effects sections, in part due to limited testing and also due to the abstract nature of this screening level assessment. The exposure section of analysis could be improved by providing field data to corroborate the models graphite deposition concentrations. Testing to evaluate the fate of graphite in soil and the specific environment in general would add to the data necessary for exposure profile analysis.

Uncertainty in characterization of ecological effects could be lessened with the accumulation of additional stressor-response data using appropriate measurement endpoints, indicator species, and graphite concentrations appropriate to produce a response in toxicity assessment testing. However, testing to date has shown only very limited response, if any at all. The relative non-toxicity of the graphite material makes stressor-response profiles essentially flat at the NOEL. A more toxic material would actually make it easier to show stressor-response profiles.

## **5.2           Risk Description**

Risk description has two primary elements. The first is the ecological risk summary, which summarizes the results of the risk estimation and uncertainty analysis and assesses confidence in the risk through a discussion of the weight of evidence. The second element is interpretation of ecological significance, which describes the magnitude of the identified risks to the assessment endpoint.

### **5.2.1       Ecological Risk Summary**

To date there is no indication of significant adverse impact to terrestrial environments from dissemination of graphite flake material as an IR screener. However, that is not to say that there is no adverse impact in all environments. This ERA is intended as a screening level assessment. The environment considered here is very generic, the plant and animal testing employed are most representative of northern temperate grasslands. These findings should not be extrapolated to more extreme environments like high altitude, northern tundra or tropic environments. Testing in these areas should include some site specific toxicity screening.

Normally, entrance into the Ecological Risk Assessment procedure is triggered by an observation of some significant adverse impact or the identification of the presence of a material or activity known to cause significant adverse impact. For graphite obscurant materials this is not the case. The driving force behind this ERA may be negative impact caused by other smoke materials that were tested and fielded without any preliminary environmental toxicity testing. Historically, almost all the smoke materials used to date have had adverse impact, which is why graphite toxicity testing and this ERA is being conducted in advance so that we know the potential environmental consequences of our actions with data to back up our decisions.

Currently there is evidence that indicates that graphite material poses little or no threat to terrestrial environments. Graphite is much less toxic than previous smoke materials, including the phosphorous smokes, HC, or brass, one of the earliest IR obscurant materials. Testing has documented the extremely low toxicity of graphite (Thompson et al., 1986; Phillips and Wentsel, 1990; Bowser et al., 1990; Driver et al., 1993). The weight of evidence in support of the findings of no significant effect is still limited to plants and earthworms. To date there is no corroborative evidence in support of the deposition model proposed by Driver et al. (1993). Also there's no documented work on the fate of graphite in the terrestrial environment. We need to answer the question of what happens over extended periods to the graphite that is deposited to the soil surface. To date the only information available is from testing with brass flakes and graphite fibers. Brass material has been shown to break down when in contact with soil (Wentsel and Guelta, 1986), but it has been indicated that graphite is much more stable (Dolezal et al., 1989) and may not become incorporated or even available through soil chemical and biological processes.

## 5.2.2 Ecological Significance

The toxicity data presented in this ERA is scientifically sound. Methodology employed is accepted by the scientific community and follows guidelines suggested by EPA. While there are only several studies documented, the evidence is substantial in support of a finding of No Observable Effect Levels in plant and earthworm toxicity testing. The deposition model employed by Driver et.al, (1993) may represent concentrations higher than actually experienced in the field. However, these possibly higher than expected concentrations are still several magnitudes lower than concentrations used in toxicity testing. Toxicity testing at these higher exposure levels showed no observable effect. Given these findings, and within the intended limits of this ERA, it is very reasonable to predict that there would be no effect from dissemination of graphite particles at field-use levels into a terrestrial environment.

### 5.2.3

### **Recommendation of Additional Testing Requirements**

In order to conduct an even more scientifically sound Environmental Risk Assessment for the effects of graphite smoke material in the environment the following environmental testing is recommended if/when such an increased need exists:

- Field tests that corroborate the dissemination and deposition rates presented in the model proposed by Driver et al., 1993, or any model that may include more site specific dissemination, meteorologic, and site specific parameters.
- Laboratory or field tests that assess the movement or fate of graphite flakes in the terrestrial environment, including material resuspension and migration and incorporation of graphite flake material in soil chemical and biological activities.
- Laboratory or field tests that document the effect of graphite material deposited to plant foliar surfaces in measurable surface concentrations that produce an observable effect, if possible, even if the effect is only temporary.
- Laboratory or field tests that document any effect of graphite on soil microbial activity. That includes graphite material deposited to the soil surface and soil amended with graphite flake material.
- Laboratory or field tests that measure the effect of graphite flake material on wildlife in the area affected by large area screening testing.
- Laboratory or field testing that documents the effects of graphite on the types of insects or arthropods that are common to terrestrial environments.

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## Literature Cited

Bowser, L.K., Phillips, C.T., and Wentsel, R.S., "Toxicity of Graphite Flakes in Soil to Earthworms", CRDEC-TR-129, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD., June 1990.

Dolezal, B., Guelta, M. A., Wentsel, R.S., "Fate of EA 5968 in Soil Cores", CRDEC-TR-073, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD., June 1989.

Driver C.J., Ligotke, M.W., Landis, W.G., Downs, J.L., Tiller, B.L., Moore, E.B., and Cataldo, D.A., "Environmental Health Effects Review for Obscurant Graphite Flakes" ERDEC-CR-056, July 1993.

Driver, C.J., Ligotke, M.W., Bowers, J.F., and Moore, E.B., "Environmental Assessment: Generator, Mechanical, Smoke: For Dual-Purpose Unit, XM56, Yuma Proving Ground, Yuma Arizona", PNL-7781, Pacific Northwest Laboratory, Richland, Washington, Oct. 1991.

EPA/630/R-92/001, "Framework For Ecological Risk Assessment", Risk Assessment Forum, U.S. Environmental Protection Agency, Washington, DC. February 1992.

EPA, "Environmental Effects Test Guidelines", EPA 560/6-82-002, U.S. Environmental Protection Agency, Washington, DC, 1982

Guelta, M.A., Banks, D.R., and Grieb, R.S., "Particle size Analysis of Graphite Obscurant Material From an XM56 Smoke Generator", ERDEC-TR-053, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD., April 1993.

Phillips, C.T., and Wentsel, R.S., "The Effect of Graphite Flakes in soil on Terrestrial Plants", CRDEC-TR-217, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD., Sept. 1990.

Wentsel, R.S., and Guelta, M.A., "The Fate of Brass Powder in Soils", CRDEC-TR-86040, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD., May 1986.

Sadusky, M, Unpublished data, "Effect of Graphite flake aerosol on Plants through direct foliar deposition", 1991-92.

Savage, J.J., "Smoke Research at CRDEC", in Proceedings of the Smoke/Obscurants Symposium XIV Volume I, CRDEC-CR-092, U.S. Army Chemical Research,

Development and Engineering Center, Aberdeen Proving Ground, MD., A. Depak and W. Klimek, ed., pp. 3-6, November 1992, Unclassified Report.

Suter, G.W., Barnthouse, L.W., Bartell, S.M., Mill, T., Mackay, D., and Paterson, S., "Ecological Risk Assessment" Lewis Publishers, Chelsea, Michigan. 1993.

Thompson, S.A., Bergman, J.D., Burnett, D.C., Carpin, J.C., Crouse, C.L., Hilaski, R.J., Infiesto, B., and Lawrence-Beckett, E., "Comparative Inhalation Screen of titanium Dioxide and Graphite Dust. CRDEC-TR-88161, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD., 1986.

Thompson, S.A., Crouse, C.L., Burnett, D.C., and Hilaski, R.J., "Repeated Inhalation Toxicity Study of Synthetic Graphite in Rats", Toxicologist 8:252, 1988.

U.S. Army Corps of Engineers, "A Report on the Accumulation of Contaminants in Soil Samples From Test Area C52-A in Connection With Smoke Weeks XIII and XIV, Eglin air Force Base, Florida", U.S. Army Corps of Engineers, Mobile District, Planning and Environment Division, Mobile Alabama, March 1993.